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This is a multi-investigator program, involving an integrated theory and modeling, synthesis, nonlinear optical spectroscopy, and electronic characterization effort, that is being undertaken by the Perry, Bredas, Kippelen and Marder gorups. The activities being pursued under this AFOSR program are: 1) development two-photon absorbing molecules with large two-photon cross sections and excited-state absorption cross sections for optical power limiting applications, 2) chromophore/nanoparticle assemblies with enhanced nonlinearity for optical power limiting applications, and 3) advanced organic transport materials for photovoltaic/photoconducting applications.

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Nanocomposite Materials and Microstructured Devices for Optical Limiting and Switching and Photovoltaic Applications

Final Report for

Dr. Charles Lee

Air Force Office of Scientific Research

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Summary

This is a multi-investigator program, involving an integrated theory and modeling, synthesis, nonlinear optical spectroscopy, and electronic characterization effort, that is being undertaken by the Perry, Brédas, Kippelen and Marder groups. The activities being pursued under this AFOSR program are: 1) development two-photon absorbing molecules with large two-photon cross sections and excited-state absorption cross sections for optical power limiting applications, 2) chromophore/nanoparticle assemblies with enhanced nonlinearity for optical power limiting applications, and 3) advanced organic transport materials for photovoltaic/photoconducting applications.

Two-Photon Materials
Progress:

1) **Theoretical Modeling:** We have made progress towards developing an understanding of the influence of the conjugated backbone and the ground-state polarization on the TPA response as well as of the influence of correlation effects. We have performed calculations of the evolution of the two-photon cross section as a function of the ground-state polarization using highly correlated quantum chemical methods (INDO/MRD-CI) for a series of symmetric and asymmetric compounds. We are developing methodologies to handle nondegenerate TPA.

2) **TPA Materials for Optical Limiting:** New centrosymmetric branched structures with a donor-acceptor donor (D-A-D) motif that contain a pyrazine linker have been synthesized and their nonlinear optical transmission and optical limiting properties have been measured. Branching appears to strongly influence the strength of the excited-state absorption at the two-photon pumping wavelength.

3) **Dye Coated Nanoparticle Synthesis and Characterization:** Thiolated two-photon dyes (A-π-A and D-π-D) have been synthesized and used to form a dense coating containing ~2,500 chromophores on silver nanoparticles and the linear and two-photon properties of the coated nanoparticles were determined. Very strong, optical limiting at low input pulse energy was observed for suspensions of silver nanoparticle clusters in solution. Attempts to date to observe strong optical limiting in dye coated nanoparticle systems have not been successful. More work is needed to stabilize the suspensions in organic solvents and to optimize resonance coupling of the dyes and the particles.

4) **TPA dye synthesis:** Some highly soluble two-photon dyes, including a liquid dye, and polymerizable dyes have been synthesized.

5) **Modeling of Two-Photon Absorbing Chromophores:** We have performed theoretical calculations on two-photon absorbing chromophores in order: (i) to understand the influence of metal cations on the donor abilities in donor-acceptor-donor systems; and (ii) to determine the influence of intermediate state resonance effect (ISRE) for non-degenerate TPA. We implemented the non-degenerate Sum-Over-States expression into our SOS program in order to calculate the resonance enhancement of the TPA cross-section. We are also in the process of developing size-consistent theoretical methods to investigate the conjugation-length dependence of TPA.

6) **Two-photon Characterization of Materials from AFRL and UCSB:** We have performed extensive meaurements of the one- and two-photon optical properties of paracyclophane linked bi-chromophore two-photon materials that were synthesized by Gui

Bazan's group at UCSB and of two AF two-photon dyes and a platinum polyyne compound synthesized at AFRL.

Important Accomplishments/Impact:

1) Calculated trends for the two-photon cross section give a guide for the design of optimized two-photon chromophores. Preliminary calculations performed on chromophores from Kevin Belfield's group at CREOL indicate that optimization of the non-degenerate photon energies can lead to an enhancement of the cross-section for the lowest TPA peak by an order of magnitude.

2) Calculations of aza-crown-ether substituted distyrylbenzenes complexed with Mg^{+2} ions indicate that there occurs a significant reduction in TPA cross-section as well as a blue shift of the lowest energy band with regard to the uncomplexed system. These findings are fully consistent with the experimental results from the Perry Group. The theoretical results are being used to design new ion sensing chromophores as well as to assess the impact of the functionalization of TPA chromophores. A manuscript on this topic has been submitted to JACS.

3) The calculated TPA cross-sections for degenerate and non-degenerate processes are in excellent agreement with the experimental data coming from the Van Stryland Group at CREOL, University of Central Florida. Nondegenerate TPA provides for a resonance enhancement of TPA cross-sections by a factor of three to four in D-π-A and D-π-D fluorene derivatives. According to a simple analysis based on the three-state model, the detuning energy between the one-photon transition energy and one of the fundamental photon frequencies is here the crucial quantity responsible for the intermediate state resonance enhancement (ISRE).

4) Centrosymmetric branched structures with a D-A-D motif show a very large effective two-photon cross section (33,000 x 10^{-50} cm^4 s $photon^{-1}$) in the near IR (800 nm), which is an order-of-magnitude increase over the state-of-the-art for D-A-D compounds. These compounds offer very strong optical limiting properties in the near IR spectral range.

5) Chromophore coated nanoparticles (with both A-π-A and D-π-D dyes) show a huge per particle cross section of about 200,000 x 10^{-50} cm^4 s $photon^{-1}$, which is a linearly additive contribution from the dyes. We have learned that two-photon plasmon resonance coupling doe s not lead to large enhancements of the dyes propertied when coupled to individual nanoparticles. This has resulted in a new strategy for improved resonance coupling to the the plasmons and potential enhancement of the dye two-photon properties. A paper on this work has appeared in JACS and others will be submitted.

6) The highly soluble two-photon dyes with large two-photon cross sections have been developed in order to maximize the optical limiting performance in device application. The optical limiting response has been shown to scale with the dye concentration. These compounds have been sent to Dr. Paul Fleitz for device related testing at Wright Laboratory.

7) Sudies on the paracyclophane linked bi-chromophore two-photon materials that were synthesized by Gui Bazan's group at UCSB show that the two-photon properties are roughly additive in the number of coupled units and that the excitonic coupling of the two-photon states is much smaller than that for the one-photon states, which we attributed to reduced transition dipole coupling for the two-photon states. The 5-ring and 7-ring dyes linked by

paracyclophanes show very broad and strong two-photon absorption covering a very large bandwidth of 150 nm in the near-IR. A manuscript on this work has been submitted to JACS.

Organic Photovoltaic/Photoconducting Materials

Progress:
1) We have demonstrated solar cells with discotic liquid crystals materials that show good transport characteristics.
2) A reduction in series resistance was observed upon transition from the isotropic phase to the columnar discotic phase for a copper phthalocyanine discotic liquid crystal former.
3) Soluble semiconductor quantum dots have been synthesized and doped into organic photoconductors with matched energy levels.
8) We have demonstrated photorefractivity at 1.5 micron using two-photon sensitizer.

Important Accomplishments/Impact:
1) A proof of concept demonstration of an organic photovoltaic cell has been performed. There is potential for light-weight deployable solar cells on plastic substrates that are environmentally friendly.
2) Fabricated CdSe and PbS sensitizers with red and infrared response. CdSe QDs in a photorefractive polymer composite showed, for the first time, overmodulation of the diffraction efficiency and response times < 100 ms. There is potential application in real time signal processing in the near infrared.
3) Two-photon photorefractive materials at 1.5 microns have allowed for the demonstration of nondestructive read-out and image reconstruction experiments.


A detailed account of the progress in two-photon materials and a summary of statistical information from this program are provided below.

Materials for Optical Limiting in the Near-Infrared Spectral Range

Various chromophores were screened as possible optical limiters in the 690-860 spectral range. Most of these chromophores are constituted by a phenylene-vinylene conjugated backbone and are symmetrically substituted with electron donor and/or acceptor groups. The materials were tested in solution (typical concentrations: 10^{-3} - 10^{-2} M), using cuvette of 1 cm pathlength. The excitation was provided by a tunable optical parametric oscillator pumped by a Q-switched Nd:YAG laser. The laser pulses produced have a duration of approximately 6 ns and a repetition rate of 10 Hz. The optical set-up had approximately an f/100 focusing geometry and the laser beam was collimated into the sample. For all the molecules studied, the mechanisms believed to be involved in the limiting response are two-photon absorption followed by excited state absorption or other resonant multi-photon absorption processes.

A brief summary of the results obtained is given below. The values of the nonlinear transmittance (T_{nlin}) reported are given by the ratio of the transmittance measured at the highest incident energy investigated (900-1000 µJ) to the linear transmittance.

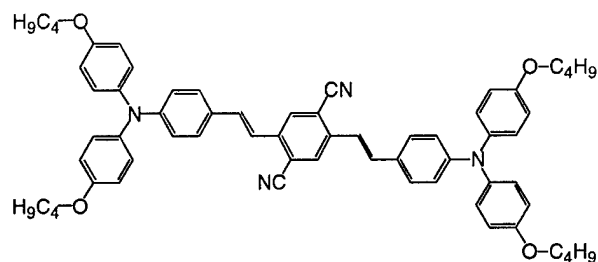**Compound #41:**
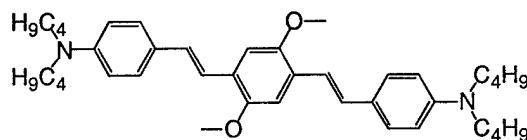
Results for a 9.6×10^{-3} M solution in toluene:

λ_{exc} = 730 nm: T_{nlin} = 0.79

750 nm: 0.82

775 nm: 0.88

Results for a 9.1×10^{-2} M solution in toluene:

λ_{exc} = 730 nm: T_{nlin} = 0.50

760 nm: 0.45

From the results on the second solution above, it has to be noted that the limiting response for this molecule is more significant at 760 nm than at 730 nm, even if the two-photon cross sections is larger at 730 nm (900 GM vs. 600 GM)[Rumi, 2000 #165], clearly indicating that other phenomena are involved in the material response to this type of excitation.
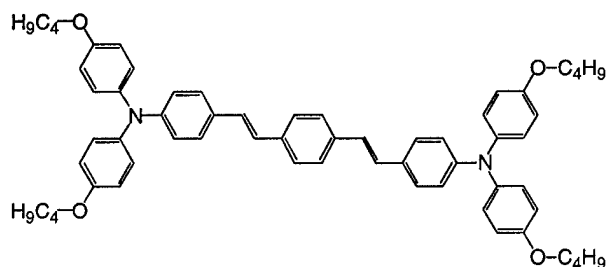
Compound #122:

Results for a 1.2×10^{-2} M solution in toluene:

λ_{exc} = 800 nm: T_{nlin} = 0.73

           830 nm: 0.77

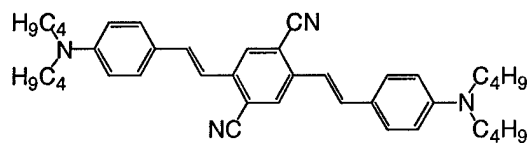**Compound #123:**

Results for a 9.7×10^{-3} M solution in toluene:

λ_{exc} = 730 nm: T_{nlin} = 0.91

           750 nm: 0.83

           775 nm: 0.78

Results for a 8.5×10^{-2} M solution in toluene:

λ_{exc} = 730 nm: T_{nlin} = 0.58

           760 nm: 0.46

Compound 126:
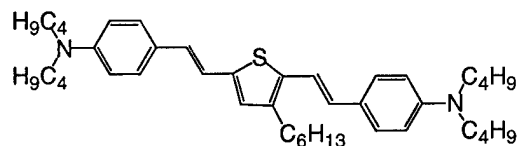

Results for a 7.8×10^{-2} M solution in toluene:

λ_{exc} = 800 nm: T_{nlin} = 0.81

           830 nm: 0.67

           860 nm: 0.80

This molecule seems to have the largest limiting behavior, in the intensity range investigated, at the same wavelength at which the two-photon peak is observed.[Pond, 2002 #1057]

Compound ThiopheneBSB:

Results for a 0.15 M solution in toluene:

λ_{exc} = 690 nm: T_{nlin} = 0.65

730 nm: 0.74

Compound 411:
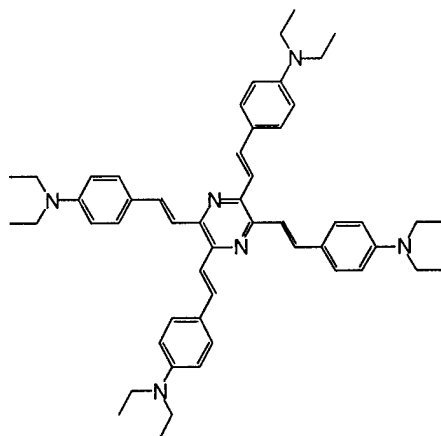
Results for a 7.8×10^{-3} M solution in dichloromethane:

λ_{exc} = 800 nm: T_{nlin} = 0.70

830 nm: 0.86

The nonlinear transmission responses of **41** and **123** at 760 nm are compared in Figure 1 below.

Figure 1. Intensity dependent transmission data for compounds **41** and 123 at 760 nm in toluene solution. The concentration of the solutions was: 0.091 M for **41** and 0.085 M for **123**.

As can be seen in the figure, both compounds exhibit rather strong nonlinear absorption, which due to two-photon induced excited state absorption.

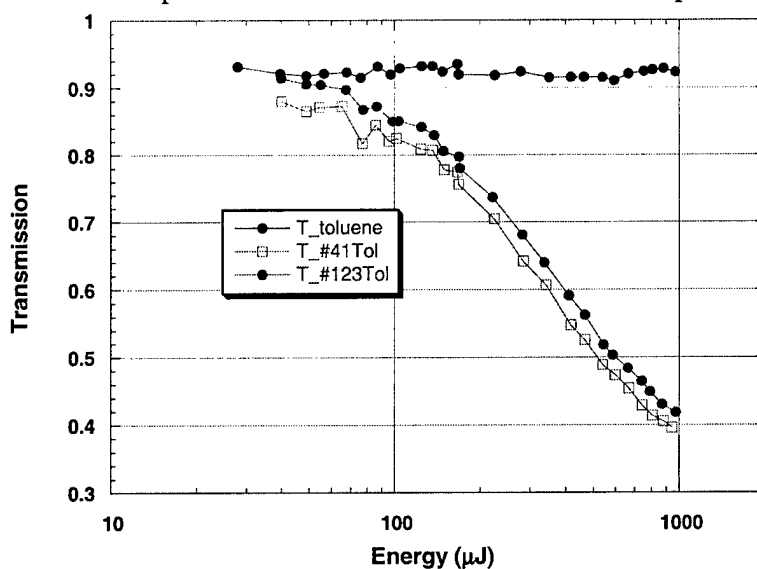The nonlinear transmission responses of **411** and **122** at 800 nm are compared in Figure 2 below.
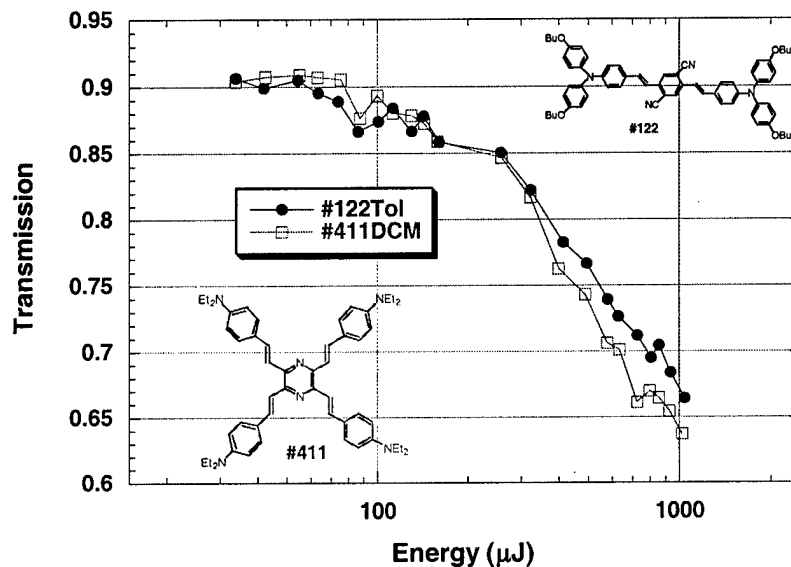
Figure 2. Intensity dependent transmission data for compounds **411** and 122 at 800 nm in dichloromethane and toluene solution, respectively. The concentration of the solutions was: ~0.008 M for **41** and 0.12 M for **122**.

It should be noted that the concentration for dye **411** is about an order of magnitude lower than for dye **122** and yet the nonlinear transmission responses are quite similar, with the response of **411** being slightly stronger. The effective two-photon absorption cross section derived for **411** is about 33,000 cm^4 s $photon^{-1}$, which is an order of magnitude larger that for other two-photon dyes that we have examined in this spectral range.

Characterization of Two-Photon Absorbing Materials: AFRL and UCSB dyes

During the course of this program, we measured the two-photon excitation spectra and determined the two-photon absorption cross sections of chromophores developed in other research laboratories. Described below are the results on:

1) Three chromophores obtained from Paul Fleitz at the Wright Patterson Air Force Research Laboratory; two of these chromophores contain donor and acceptor groups linked through a conjugated bridge in a linear or trifold symmetric arrangement while the third chromophores is a platinum-containing poly-yne. The main goal of this investigation was the extension of the characterization of these molecules to a wide wavelength range (715 – 890 nm), as only their two-photon properties around 800 nm have been previously reported;

2) Five chromophores synthesized in the group pf Prof. Guillermo Bazan at the University of California, Santa Barbara. Three of these molecules are constituted of two donor-substituted phenylene-vinylene oligomers linked in their central portion thorough a [2.2]paracyclophane unit; the other two molecules are linear counterparts to the paracyclophane chromophores. The purpose of the work was the comparison of the spectroscopic properties of the linear and dimeric chromophores and the investigation of the interaction between the two arms of the dimer through the paracyclophane unit.

## 1) AFRL dyes

The molecules we received from the Air Force Research Laboratory at Wright-Patterson are the following:

1) AF240 (linear D-π-A chromophore, with D = diphenyl-amino and A = benzothiazole):

AF240
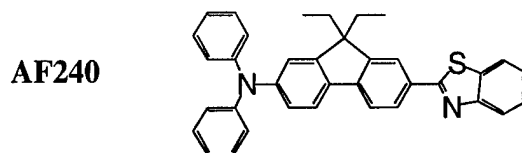
2) AF350 (three arm D-A$_3$ chromophore with a central N atom and three identical units attached to it, each containing a conjugated bridge and a benzothiazole acceptor):

AF350
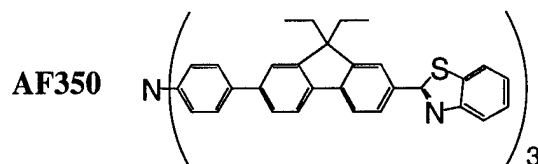
3) PE2 (a platinum containing poly-yne, whose exact structure has not been provided to us at the time of the measurements; since then a paper on the photophysical properties of this and other Pt-containing oligomers has been published[2] and the structure reported there is as follows):
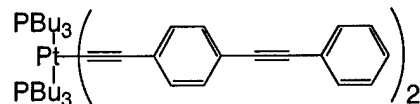
Linear Specroscopy

UV-Visible absorption spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer. Corrected fluorescence spectra were collected on a Spex Fluorolog-2 spectrofluorimeter. Quantum yields, η, of dilute solutions were determined using quinine bisulfate in 1 N H_2SO_4 ($\eta = 0.55$) or bis-o-methyl-styrylbene ($\eta = 0.94$) as reference compounds.

Figs. 1 and 2 display the absorption and fluorescence emission spectra of compounds AF240 and AF350. The measurements were performed in toluene and in tetrahydrofuran (THF). The absorption band peaks at 393-394 nm for both AF240 and AF350. In either case, the shape and strength of the absorption band are very similar in toluene and THF (see also Table 1). The fluorescence spectra, instead, exhibit a solvent dependence, with the spectrum in THF being less structured and red-shifted with respect to the one in toluene. Some discrepancies have been observed with the results reported in the literature on these molecules. In particular, our estimate
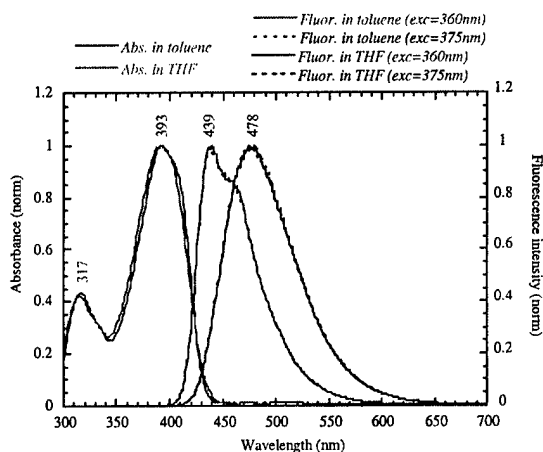
Fig. 1: Absorption and fluorescence emission spectra of AF240 in toluene and THF.
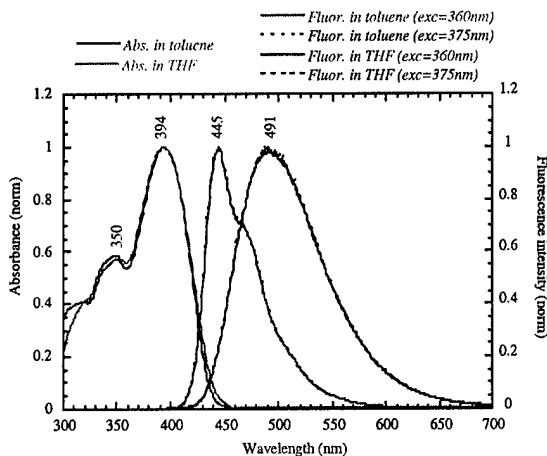

Fig. 2: Absorption and fluorescence emission spectra of AF350 in toluene and THF.

of the extinction coefficient for AF350 is much lower than the one in He *et al.*[3] (as obtained from inspection of the spectrum in Fig. 2 of that paper, which refers to a concentration of 1×10^{-4} M). Our measurement has been repeated more than once on solutions with concentrations in the

range $10^{-6} - 10^{-4}$ M (a 0.1 cm cuvette was used for the higher concentration solutions). It has to be noted that, if our estimate ($\approx 1.5 \times 10^5$ M^{-1} cm^{-1}) is correct, ε_{max} for AF350 is roughly three times that of AF240, which seems reasonable in view of the structure of AF350 (even if each arm of AF350 contains one additional phenylene with respect to AF240). Both molecules are highly fluorescent in toluene as well as in THF ($\eta > 0.8$).

The absorption spectrum of PE2 (Fig. 3) shows a peak at 352 nm in toluene, with an ε_{max} of 8.8×10^4 M^{-1} cm^{-1}, effectively the same as the value reported in benzene,[2] but about 14% larger than in THF (see Table 1).[4] This molecule is very weakly fluorescent: $\eta \approx 0.0014$ (the uncertainty in this value is about 20%). PE2 shows a peculiar emission spectrum, with two distinct bands: one peaking at 386 nm and the other around 524 nm, both with vibronic structure (Fig. 3). Except for the relative intensity of the two bands, the spectrum in Fig. 3 agrees with the one reported by Rogers et al.[2] Emission spectra with similar features have been previously observed in conjugated molecules containing heavy metals and have been interpreted as the emission from a singlet state (S_1) and a triplet state (T_1), with the triplet emission appearing at longer wavelengths.[5,6] In the case of PE2, the singlet peak area represents 70% of the total emission. The value of η given above and in Table 1 refers to the total emission (singlet + triplet). It has to be pointed out that in our measurement, the solvent was not de-oxygenated, and thus it was not possible to estimate the triplet yield. The excitation spectra obtained by
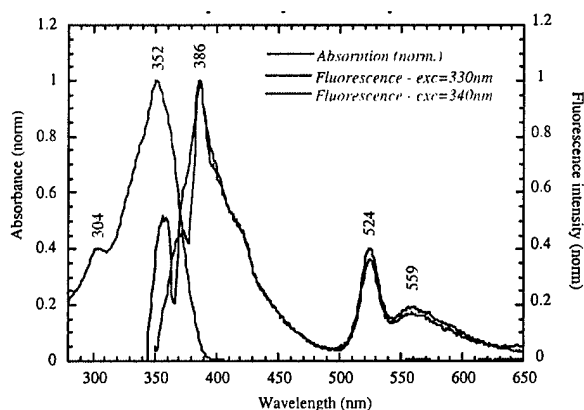
Fig. 3: Absorption (red) and fluorescence emission (blue and green) spectra of the platinum poly-yne PE2 in toluene. The excitation wavelengths used for the collection of the fluorescence spectra are 330 nm (blue) and 340 nm (green). The valleys observed at 365 and 380 nm in the two fluorescence spectra are due to over-subtraction of the solvent Raman band.
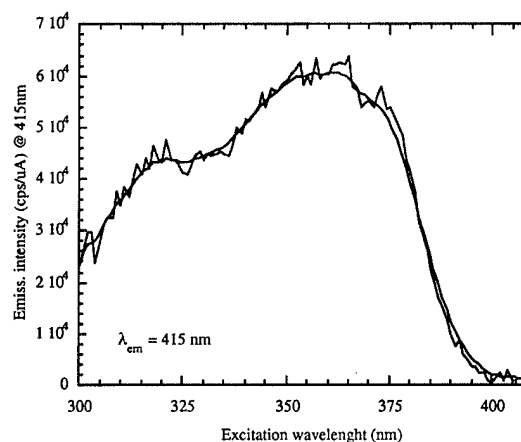
Fig. 4: Fluorescence excitation spectrum of the platinum poly-yne PE2 (detection wavelength = 415 nm) in toluene. The blue line is an interpolation of the actual experimental points (red).

monitoring the emission at 415 nm (Fig. 4) and 525 nm are very similar (main peak at 360 nm, secondary peak at 320 nm) and resemble -- but are not identical to -- the absorption spectrum.

Table 1: Linear spectroscopic parameters for AF240, AF350, and PE2. Literature values, where available, are included for comparison. $\lambda^{(1)}_{max}$ = peak in the linear absorption spectrum; ε_{max} = extinction coefficient at $\lambda^{(1)}_{max}$; λ_{fl} = peak in the fluorescence emission spectrum; η = fluorescence quantum yield; (sh) = shoulder in the absorption or fluorescence spectrum.

| Compound	Reference	$\lambda^{(1)}_{max}$ (nm)	ε_{max} (M^{-1}cm^{-1})	λ_{fl} (nm)	η
AF240 (toluene)	this study	393 317	4.82×10^4	439 460 (sh)	0.87 (a)
AF240 (THF)	this study	393 317	4.54×10^4	478	0.87 (a)
AF240 (THF)	[7]	391.5	$\approx 4.4 \times 10^4$	479	
AF350 (toluene)	this study	394 350	1.45×10^5	445 470 (sh)	0.82 (a)
AF350 (THF)	this study	394 350	1.56×10^5	491	0.80 (a)
AF350 (THF)	[3]	≈ 400	2.7×10^5	≈ 480	
PE2 (toluene)	this study	352 304	8.8×10^4	385 420(sh) 524 559	0.0014 (b)
PE2 (benzene)	[2]	355	8.9×10^4	395	0.001
PE2 (THF)	[4]	353	7.71×10^4		

(a) Excitation wavelength: 370 nm; quantum yield reference: quinine bisulfate in 1 N H_2SO_4 ($\eta = 0.55$).

(b) Excitation wavelength: 330 and 340 nm; quantum yield reference: bis-o-methyl-styrylbenzene in cyclohexane ($\eta = 0.94$).

Two-Photon Spectroscopy

The two-photon absorption cross-sections, δ, were determined by a relative measurement using the two-photon induced fluorescence method.[8] The reference standards used were fluorescein (in pH 11 water) and coumarin 307 (in methanol).[8] The excitation source used for the two-photon induced fluorescence experiment was a Ti:Sapphire laser (Tsunami, Spectra-Physics), which generates ~100 fs pulses at a repetition rate of 82 MHz. The excitation wavelength range covered in this study was 715 - 890 nm. The same experimental set-up as described in Beljonne

et al.[9] has been used in this study. The concentration for the solutions studied was in the range 7 $\times 10^{-6} - 7 \times 10^{-5}$ M. The two-photon induced fluorescence signal was collected at λ_{det} = 520 nm.

A summary of the results is given in Table 2 and the complete two-photon spectra are displayed in Fig. 5 (AF240), Fig. 6 (AF350), and Fig. 7 (PE2). As expected, AF240 and AF350 show a two-photon peak around 800 nm, that represents a transition into the same electronic state (S_1) responsible for the linear absorption spectrum ($\lambda^{(2)}_{max} \approx 2 \lambda^{(1)}_{max}$). However, in the case of AF350, large values of δ (up to 1000 GM) are observed also in the blue region of the spectrum (< 750 nm). The peak in this region is located at, or below, 715 nm, the shortest wavelength investigated. The two-photon absorption in this range could arise from the state responsible for the linear absorption at 350 nm. A state in this energy range is not visible in the linear absorption spectrum of AF240 and this molecule exhibits only one band in the two-photon excitation spectrum in the range investigated. Of particular interest is the fact that AF350 exhibits relatively large two-photon cross sections ($\delta \geq$ 200 GM) over a broad wavelength range (715 - 850 nm in THF). The complex characteristics of the two-photon spectrum of AF350 clearly evidence the importance of investigations spanning over wide wavelength ranges.

No significant solvent dependence is observed for AF240, while the δ values for AF350 in THF are at least 20% larger than in toluene (but the ratio between the values in toluene and THF is not constant with wavelength). Our estimate of δ for AF350 is about a factor of three larger than the one reported in the literature and obtained by z-scan measurements.[3] At this point, the reason for this discrepancy is not clear, but it has to be kept in mind that the measurement of nonlinear optical properties of materials is still affected by relatively large uncertainties (about 15% in our experiment).

The results reported for PE2 in Table 2 and Fig. 7 are to be considered only a rough estimate of the two-photon cross section of this chromophore. Due to the very low quantum yield and the relatively small δ ($\approx$ 20 GM), the two-photon induced fluorescence signal was very close to the detection limit of our instrument, even when the full power of the laser was used for the excitation. However, the results obtained are consistent with the presence of a state around 350 nm (3.5 eV), as observed in the linear absorption spectrum. A second detection wavelength (400 nm, in the singlet emission peak) was also used in the measurement on PE2. The results, which are included in Fig. 7, are smaller that those obtained for λ_{det} = 520 nm (in the triplet emission peak). This could indicate that the ratio between the singlet and triplet emission is different after two-photon than after one-photon excitation or depends on the specific sample conditions (such as the amount of oxygen present). The results reported here were obtained assuming that the shape and relative intensity of the two emissions are unchanged and using the value of 0.0014 for the overall quantum yield. The difference observed could also be due simply to the large

uncertainty in the measurements itself. Further experiments would be necessary to substantiate or modify these assumptions.

Table 2: Two-photon spectroscopic parameters for AF240, AF350 and PE2. $\lambda^{(2)}_{max}$ = peak of the two-photon induced fluorescence spectrum; δ_{max} = two-photon absorption cross section at $\lambda^{(2)}_{max}$ (values are rounded to the closest 5 GM). Fluorescein and coumarin 307 were used as standards. Results reported in the literature, where available, are included for comparison. 1 GM = 1 × 10^{-50} cm^4 s /photon-molecule.

Compound	Reference	$\lambda^{(2)}_{max}$ (nm)	δ (GM)	$\lambda^{(2)}_{max}$ (nm)	δ (GM)
		Standard = fluorescein (*)		Standard=coumarin (*)	
AF240 (toluene)	this study	820	140	810	125
		800 (a)	120	800 (a)	115
AF240 (THF)	this study	820	150	810	135
		800 (a)	130	800 (a)	125
AF240 (THF)	7	800 (b)	9800 (NLT, 8 ns)		
AF350 (toluene)	this study	820	310	810	310
		≤ 715	840	≤ 715	540
		800 (a)	330	800 (a)	310
AF350 (THF)	this study	820	455	810	430
		≤ 715	1035	≤ 715	665
		800 (a)	450	800 (a)	420
AF350 (THF)	3	796 (b)	152 (z-scan, 135 fs)		
		810 (b)	37000 (NLT, 7 ns)		
PE2 (toluene)	this study	≤ 715	≈ 25	≤ 715	≈ 15

(*) Standard applies only to results from this study.
(a) Not a peak (value given for comparison with literature).
(b) Single wavelength measurement.

Fig. 5: Two-photon spectrum of AF240 in toluene (triangles) and THF (circles). The reference TPA chromophores used were fluorescein (red symbols) and coumarin (blue symbols).

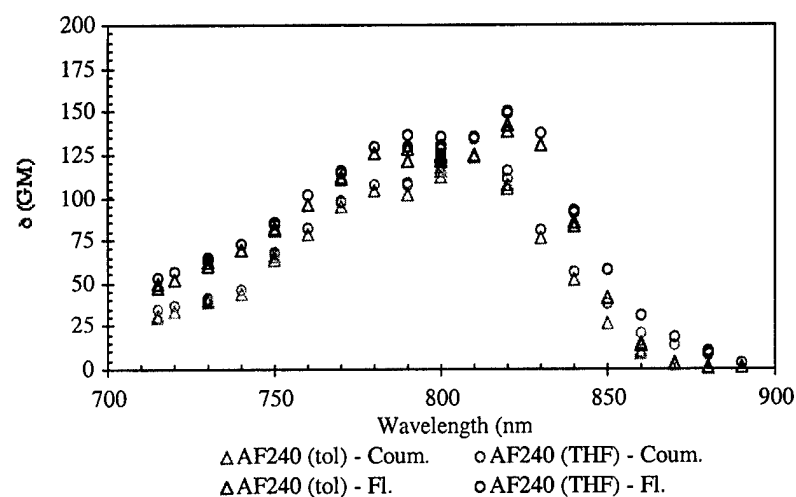Fig. 6: Two-photon spectrum of AF350 in toluene (triangles) and THF (circles). The reference TPA chromophores used were fluorescein (red symbols) and coumarin (blue symbols).
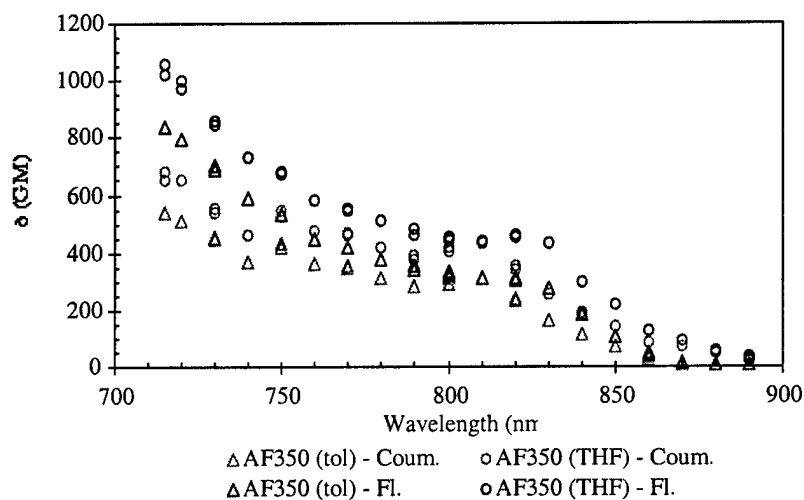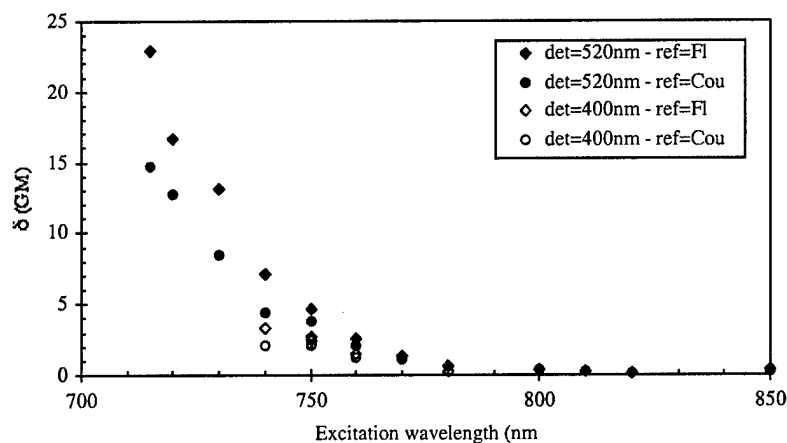

Fig. 7: Two-photon spectrum of PE2 in toluene. The measurements were performed detecting the fluorescence emitted at 400 nm (open symbols) and 520 nm (close symbols). Fluorescein (diamonds) and coumarin (circles) were used as references.

Conclusions

The one-photon and two-photon properties of three chromophores synthesized at the Air Force Research Laboratory at Wright-Patterson have been studied. AF240 shows a two-photon absorption peak around 810 nm, with a cross section of about 150 GM. AF350 exhibits a peak at 820 nm ($\delta \approx 450$ GM) and another at, or below, 715 nm ($\delta \approx 1000$ GM). As a result of the presence of these two bands, AF350 shows a relatively large two-photon absorption over a broad wavelength range. Both AF240 and AF350 are highly fluorescent in toluene and tetrahydrofuran, and show similar one and two-photon spectra in the two solvents. On the other hand, PE2 has very low quantum yield and low two-photon cross section ($\delta \approx 20$ GM at 715 nm).

2) Paracyclophane Linked Two-Photon Dyes

The molecules characterized during this study are *bis*(1,4)-(4'-dihexylaminostyryl)benzene (**3R**), tetra(4,7,12,15)(4'-dihexylaminostyryl)[2.2]paracyclophane (**3R$_D$**), bis(1,4)-(4"-(4'-dihexylaminostyryl)styryl)benzene (**5R**), tetra(4,7,12,15)-(4"-(4'-dihexylaminostyryl)styryl)[2.2]paracyclophane (**5R$_D$**) and tetra(4,7,12,15)-(4'''-(4"-(4'-dihexylaminostyryl)styryl)styryl)[2.2]paracyclophane (**7R$_D$**) and are depicted in Fig. 8. Quantum chemical calculations on these chromophores were performed by Sergei Tretiak, at the Los Alamos National Laboratory using the time-dependent Density Functional Theory technique, interfaced with the Collective Electronic Oscillator program. A manuscript describing the results of this study has been submitted to the J. Am. Chem. Soc.[10]
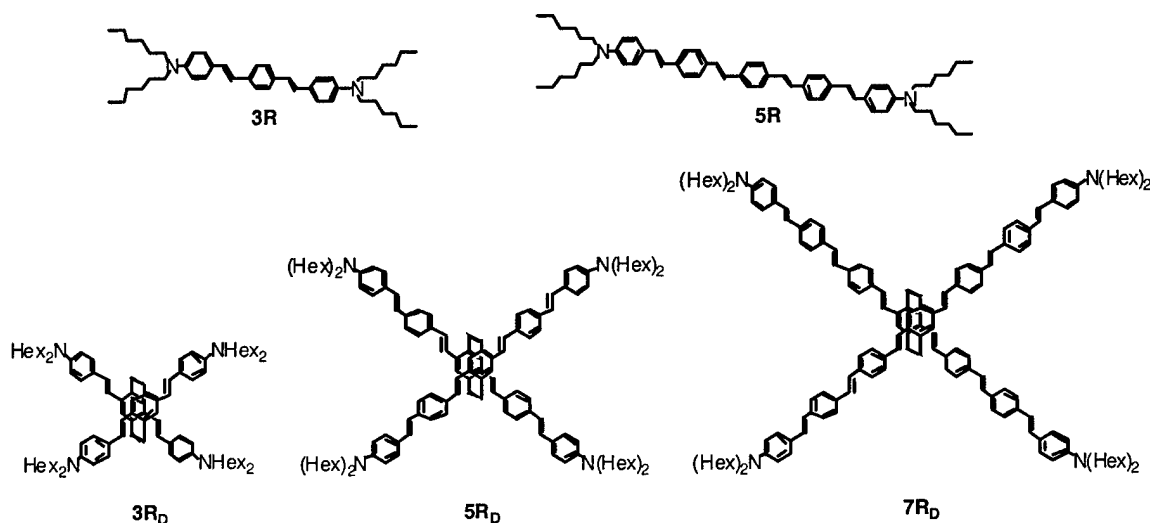

Fig. 8: Molecular structure of the two-photon chromophores synthesized by Prof. G. Bazan's group at the University of California, Santa Barbara.

Linear Spectroscopy

The absorption and emission spectra of the linear and the corresponding paracyclophane (pCp)

dimer compounds were measured in toluene. Fig. 9 shows a comparison of spectra for **3R** and **3R$_D$**. Note the red-shift of the absorption maximum of **3R$_D$** relative to **3R** (439 nm vs. 412 nm, respectively). Also, a second smaller peak appears in the absorption of **3R$_D$** at ~ 385 nm. This "Davydov-like" splitting has been observed previously in (4,7,12,15)tetra(4-*t*-butylstyryl)[2.2]paracyclophane, another dimer in which oligophenylenevinylene segments are joined *via* their central rings in a crisscross fashion.[11] The emission maximum of **3R$_D$** is also red-shifted relative to that of **3R** (490 nm vs. 453 nm, respectively).
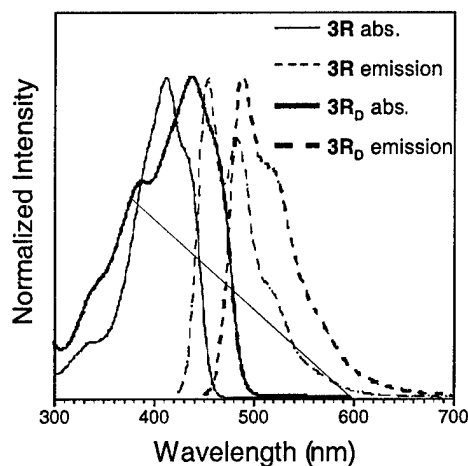

Fig. 9: Absorption and emission spectra of **3R** and **3R$_D$** in toluene. The emission spectra were obtained by exciting at the corresponding absorption maxima.

The trends observed in the three-ring compounds are repeated in the five ring models (Fig. 10). The absorption of **5R$_D$** is red-shifted by 22 nm (0.14 eV) relative to **5R** (457 nm vs. 435 nm respectively). The absorption spectrum of **5R$_D$** also shows a shoulder at ~ 400 nm although it is less pronounced than the splitting in the **3R$_D$** spectrum. The emission of **5R$_D$** is also red-shifted relative to **5R** (510 nm vs. 485 nm, respectively). Note the red-shift in the absorption of **5R$_D$** vs. **3R$_D$** of 18 nm (0.11 eV). As expected, increased chain length leads to increased conjugation. The absorption spectrum of **7R$_D$**, however, reveals a maximum at 454 nm, approximately the same as **5R$_D$**. It seems that the saturation value for the energy of the lowest excited state is reached for a chain length of five rings. Recent experimental studies suggest longer saturation lengths in oligophenylenevinylenes structurally similar to the molecules in this study. Torsional disorder may restrict the conjugation to five repeat units or the influence of the donor substituents on the energy of the lowest one-photon band may be diminished for the longer chain lengths. Studies of the absorption properties of these chromophores as a function of solvent and temperature, as well as studies of related compounds with, for example, different donors should be conducted to ascertain the origin of this effect.

All of the compounds in this series exhibit a high fluorescence quantum yield in toluene (η in Table 3; the quantum yields were determined relative to 9,10-diphenylanthracene in degassed spectral grade cyclohexane[12]). There appears to be a small decrease in η going from the linear to the dimer models. This decrease is consistent with an increased number of torsional degrees of freedom.
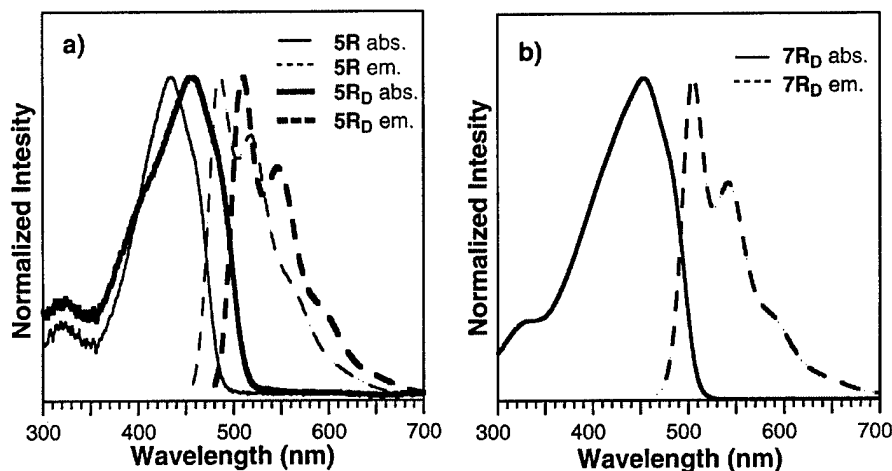
Fig. 10: Absorption and emission spectra of a) **5R**, **5R$_D$** and b) **7R$_D$** in toluene. The emission spectra were obtained by exciting at the corresponding absorption maxima.

Table 3: Summary of spectroscopic data for linear and pCp-based chromophores (in toluene). The theoretical TDDFT results are given in parentheses.

Compound	$\lambda^{(1)}_{max}$ (nm)	λ_{fl} (nm)	η	ε_{max} (M^{-1} cm^{-1}) (a)	ε_{INT} (M^{-1} cm^{-2}) (b)	M_{ge} (D) (c)
3R	412 (405)	453	0.89	8.28×10^4	3.35×10^8	11.3 (13.8)
3R$_D$	439 (434)	490	0.86	1.04×10^5	6.67×10^8	16.4 (20.3)
5R	435 (460)	485	0.92	1.27×10^5	5.40×10^8	14.7 (17.3)
5R$_D$	457 (480)	510	0.87	1.92×10^5	1.02×10^9	20.7 (28.5)
7R	(484)					(21.2)
7R$_D$	454 (495)	506	0.75	2.38×10^5	1.31×10^9	23.3 (32.1)

(a) ε_{max}: peak extinction coefficient.

(b) ε_{INT}: integral of the extinction coefficient over the main absorption band ($\int\varepsilon(\omega)d\omega$, with ω expressed in wavenumbers).

(c) M_{ge} (in Debye, D): transition dipole moment between the ground state (g) and the first excited state (e). See text for the definition of state e in the case of the dimers.

It is interesting to compare the strengths of the electronic transitions that give rise to the absorption bands. The extinction coefficients at the peak of the absorption band (ε_{max}) are reported in Table 3. It can be seen immediately that, although ε_{max} increases on going from a given linear molecule to the corresponding crisscross dimer, the magnitude of the increase is different for the 3-ring and 5-ring systems (ε_{max}(**3R$_D$**) / ε_{max}(**3R**) = 1.26 and ε_{max}(**5R$_D$**) / ε_{max}(**5R**) = 1.51). This is due to differences in the shape of the absorption band amongst both the linear molecules and the dimers. The relative intensity of the two resultant peaks of the Davydov splitting for the dimers also varies in the series. In order to take into account the contributions from both components, the extinction coefficients have been integrated over the entire absorption band ($\varepsilon_{INT} \equiv \int\varepsilon(\omega)d\omega$); this quantity is proportional to the oscillator strength of the electronic transition[13]). The results are included in Table 1 and show that ε_{INT} approximately doubles on

going from the linear to the crisscross molecules ($\varepsilon_{INT}(\mathbf{3R_D})$ / $\varepsilon_{INT}(\mathbf{3R})$ = 1.99 and $\varepsilon_{INT}(\mathbf{5R_D})$ / $\varepsilon_{INT}(\mathbf{5R})$ = 1.89). These results suggests that the contributions to the oscillator strength from the two molecules in the crisscross dimers are additive and that the interaction of the two molecules results only in a redistribution of the overall absorption strength over the two components of the splitting of the electronic band.

For the linear molecules, the absorption band is due to the electronic transition between the ground state, g, and the lowest excited state, e. The corresponding transition dipole moment, M_{ge}, can be evaluated easily and is included in Table 3. A similar approach can be used for the crisscross molecules if, for the moment, we assume that the overall absorption band is due to a single electronic transition. The values of M_{ge} found in this way appear to increase with chain length. This trend agrees well with previous results for donor-π-donor oligophenylenevinylene derivatives.[1] Specifically, in the molecules studied here M_{ge} increases approximately with the square root of the total number of double bonds (counting with each phenyl ring as 1.5 double bonds).

The quantum chemical calculations reproduce the linear absorption spectra accurately, in particular the red-shift of the absorption maximum of $\mathbf{3R_D}$ and $\mathbf{5R}$, compared to $\mathbf{3R}$. However, the absorption of $\mathbf{7R_D}$ is red shifted by ~0.2 eV in the TDDFT calculations, compared to the experiment. This discrepancy can be ascribed to geometrical distortions of the molecular backbone, which could limit the effective conjugation length or to an overestimate of the exciton delocalization with the TDDFT approach. Another feature that can be observed in both experimental and theoretical linear absorption spectra of the dimers is the strong Davydov splitting of the lowest electronic transition, due to the electrostatic interaction between the monomer transition dipoles and to the strong electronic exchange through the paracyclophane core upon dimerization ($\mathbf{3R}$ vs. $\mathbf{3R_D}$, $\mathbf{5R}$ vs. $\mathbf{5R_D}$, and $\mathbf{7R}$ vs. $\mathbf{7R_D}$). In particular, this electronic delocalization leads to an overall red-shift of the absorption band and to the appearance of both Davydov components in the linear absorption spectrum. This can be acribed to the fact that the lowest excited state of the linear chormophores (of B_u symmetry) is expected to split into two components, one of B_2 and one of B_3 symmetry (both one-photon allowed), due to the coupling of the two chromophores in the dimer and their relative orientation. We calculate splittings of 0.24, 0.17, and 0.12 eV in the spectra of $\mathbf{3R_D}$, $\mathbf{5R_D}$, and $\mathbf{7R_D}$, respectively, which we attribute mostly to dipolar interactions. The splitting decreases in the large dimers, since these have a reduced density of the excitonic wavefunction at the paracyclophane contact point, and, therefore, have a smaller interchromophore interaction.

Two-Photon Spectroscopy

The two-photon absorption cross sections (δ) were determined by the two-photon induced fluorescence method using both femtosecond (fs) and nanosecond (ns) pulsed lasers as excitation sources.[1,9] The reference standards used in this case were fluorescein (in water, pH 11)[8] and *p*-bis(*o*-methylstyryl)benzene (in cyclohexane).[14,15] The two-photon spectra of the chromophores investigated are displayed in Fig. 11 for excitation wavelengths in the range 650 - 910 nm. It should be noted that the agreement between the fs and ns data, in their overlap region, is very good for molecules $\mathbf{3R}$ and $\mathbf{3R_D}$, but less so for the other molecules. However, the data show the same trend in all cases (for example, the δ value is larger at 730 nm than at 750 for $\mathbf{5R}$ and $\mathbf{7R_D}$ according to both the ns and fs results). In addition, it has to be noted that, for an uncertainty of about 15%, *only* in the case of $\mathbf{7R_D}$ the ns and fs data lie outside each other's error bar (but they are within 2 standard deviations from each other). At present, the origin of the discrepancy

between the ns and fs data is unknown. However, the conclusions drawn from the data reported in this work are not sensitive to this uncertainty (at most a factor of 1.5). The ns measurements could even be affected by a larger uncertainty because they were conducted at lower intensities than typically used in our laboratory (by a factor of 4 or 5). This was necessary because, at some excitation wavelengths, deviations from the expected dependence of the signal on the square of the laser intensity were observed at the intensities normally used for other molecules. These deviations indicate the onset of other effects that can occur after the molecules are excited, for example excited state absorption, photoionization or other processes that slow down the ground state recovery, thus reducing the number of times each molecule can be excited during a single pulse.

The spectra of compounds **3R** and **3R$_D$** show only one peak (around 720 nm), while the other compounds clearly show two peaks, one around 720 nm, the other around 810 - 830 nm. The position of the two-photon peak at the longest wavelength (corresponding to the lowest energy transition and indicated as peak *i* in Table 4) moves to the red with increasing chain length for the linear molecules or the dimers, even if the shift is relatively small going from **5R$_D$** to **7R$_D$**, suggesting that the energy of the two-photon state has reached a saturation value for these compounds. A similar phenomenon is observed in the position of the linear absorption maximum, as described in the previous section.
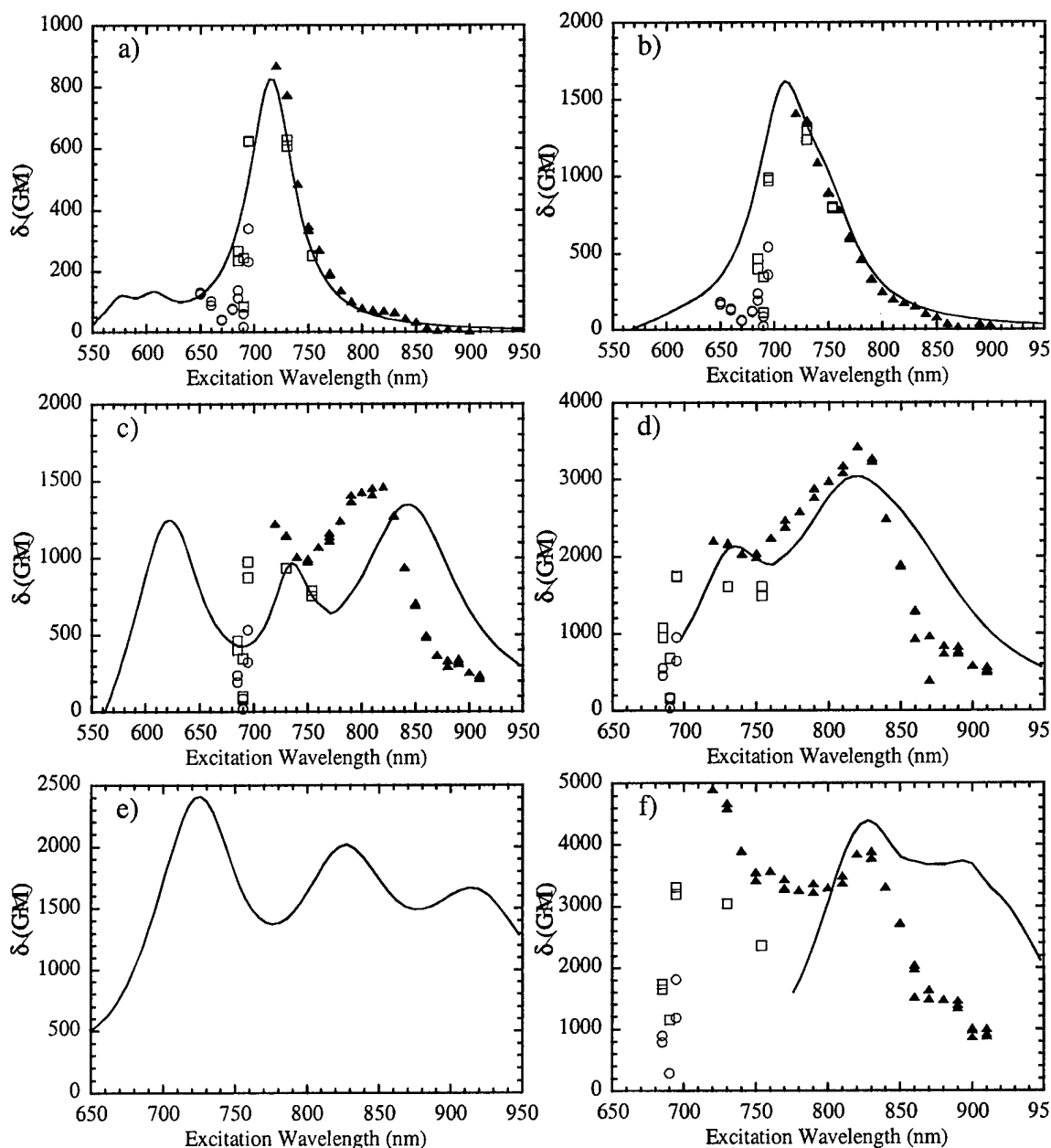
Fig. 11. Experimental and theoretical two-photon induced excitation spectra for: a) **3R**, b) **3R_D**, c) **5R**, d) **5R_D**, e) **7R**, and f) **7R_D**. Experimental results: (triangles) fs measurements using fluorescein as standard; (open squares) ns measurements using fluorescein as standard; (open circles) ns measurements using *bis*(methylstyryl)benzene as standard. Theoretical results: solid line.

Overall, the data in Table 4 show that there is an increase in the value of δ for peak i (δ_i) with increasing chain length and in going from a linear molecule to the corresponding dimer. Moreover, the δ value for peak ii (δ_{ii}) increases going from **5R**, to **5R_D** and to **7R_D**. In fact, for **7R_D**, peak ii is the strongest two-photon peak ($\delta_{ii} > \delta_i$). If the one-photon state is taken to be the intermediate state in a simplified Sum-over-States (SOS) description,[16] the large values for δ_{ii} can be explained partly by the smaller energy detuning term (≈ 1.0 eV) for the two-photon state involved in this transition with respect to the one responsible for peak i (1.2 – 1.3 eV).

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When comparing the results for the linear molecules and the corresponding criss-cross dimers, it is immediately apparent that, in contrast to the linear spectra, the general features of the two-photon spectra are similar (one peak at the same wavelength in the 3-ring case; two bands in approximately the same position in the 5-ring case). The peak δ value increases in going from the linear to the criss-cross case, but the ratio is significantly larger in the 5-ring case $(\delta_i(3R_D)/\delta_i(3R) = 1.6;\ \delta_i(5R_D)/\delta_i(5R) = 2.4)$. However, closer inspection of the shape of the spectra indicates that band of $3R_D$ is broader than that of $3R$, while the width of peaks i in $5R$ and $5R_D$ are similar. Accounting for a different band shapes leads to an effective increase of the ratio for the 3-ring case (see below). The broadness of the band in $3R_D$ could be due to the presence of two unresolved components of the main transition, a result of Davydov splitting due to the coupling between the two chromophores that constitute the dimer, similar to what was observed in the linear absorption spectra. This type of splitting is actually predicted by the quantum chemical calculations, but it is found to be small.

We can thus conclude that the two-photon cross section of the crisscross dimer is approximately twice that of the corresponding linear molecule. An increase of similar magnitude was observed for ε_{INT}. In a SOS description, this suggests that the values of δ are primarily determined by the transition moment between the ground and the first excited state (M_{ge}) and that there are only small differences in the other transition moments involved.

To compare more precisely the experimental spectra with the results of the quantum chemical calculations, it would be useful to separate the contributions of peak i and ii (due to the broadness of some of the peaks, the position and the magnitude of the maximum can be affected by the adjacent band). We thus performed a fitting of the experimental spectra using a superposition of two Gaussian band shapes. Although the results are necessarily approximate, they provide some insight into the spectroscopic properties of these chromophores. Gaussians were chosen as fitting curves for their simplicity, even if the shape of some of the experimental bands were not symmetric. Even with such approximations the resulting fits are in good for all the molecules. For completeness, a similar fitting procedure was performed on compounds $3R$ and $3R_D$, but using only one Gaussian component. Table 5 lists the significant fitting parameters

Table 4: Two-photon absorption parameters for the lowest (i) and highest (ii) energy peaks.(a)

Compound	$\lambda_i^{(2)}$ (nm) (b)	δ_i (GM) (c)	$\lambda_{ii}^{(2)}$ (nm) (b)	δ_{ii} (GM) (c)
3R	720 (715)	870 (824)	—	—
3R$_D$	720 (710)	1410 (1615)	—	—
5R	810 (845)	1450 (1345)	720 (735)	1230 (966)
5R$_D$	820 (817)	3430 (3036)	720 (734)	2210 (1938)
7R	(920)	(1652)	(828)	(2013)
7R$_D$	830 (894)	3890 (3730)	720 (828)	4910 (4390)

(a) Theoretical results are given in parenthesis. Linewidths $\Gamma = 2\ (\ln 2)^{0.5} \cdot \sigma$ (where σ's are the Gaussian widths from Table 4) have been used to estimate the theoretical magnitudes of the cross sections, except for molecule 7R, for which a linewidth of $\Gamma = 0.15$ eV has been used (see text).

(b) $\lambda^{(2)}$: position of the peak in the two-photon absorption spectrum

(c) δ: peak two-photon absorption cross section (1 GM = 1×10^{-50} cm^4 s/ photon-molecule); the uncertainty in δ is of the order of 15%.

obtained by this method.

It is immediately evident from these results that the width of the two-photon peaks *i* and *ii* for the same molecule are rather different. Some differences are also observed from molecule to molecule. Consequently, it is more useful to discuss not the amplitudes of the Gaussians (δ_0 or maximum δ values), but their areas, quantities that are related to the integrated two-photon absorption cross section for a given transition and could be compared more directly with theoretical predictions. Several conclusions can be drawn from the analysis of the band areas (Table 5). First, the area of the two-photon peaks increases by a factor of ~ 2 going from a linear molecule to the corresponding crisscross dimer. In particular: area($3R_D$) / area($3R$) = 2.0, area($5R_D$,*i*) / area($5R$,*i*) = 2.0. As suggested above, this indicates that the two-photon absorption cross section for this state is approximately additive in the two components of the dimer. Secondly, the ratio of the areas for peak *i* and peak *ii* decreases when going from $5R$ to $5R_D$ and to $7R_D$: the ratios [area(*i*) / area(*ii*)] are 2.4, 2.1 and 1.8, respectively (note that the trend is not monotonic for the amplitudes of the bands). Thirdly, the area of peak *i* depends approximately linearly on chain length. The increase in the area of peak *ii* with increasing length is instead super-linear.

It is possible to estimate the transition dipole moments between the first excited state (*e*), and the two-photon state (*e'*) corresponding to the peaks *i* or *ii*, $M_{ee'}(i)$ or $M_{ee'}(ii)$.[1] The transition moments calculated in this way correspond to orientational averages of the actual molecular transition moments. Table 5 includes the transition moments obtained if the fitting results are used as peak position, amplitude of δ and width of the peak. It can be seen that the transition moments $M_{ee'}$ are similar for a given linear molecule and the corresponding crisscross dimer (10-11 D for the 3-ring compounds, and 15-16 D for peak *i* for the 5-ring ones). This confirms the

Table 5: Fitting parameters for the two-photon spectra.

Compound		δ_0 (GM)[a]	E_0 (eV)[a]	σ (eV)[a]	area (GM x eV)[b]	$M_{ee'}$ (D)[c]
3R		805	1.723	0.075	107.0	11.0 (10.1)
$3R_D$		1320	1.704	0.093	217.7	9.5
5R	peak *i*	1456	1.550	0.119	305.9	15.9 (12.0)
	peak *ii*	1149	1.736	0.062	126.3	7.8 (6.5)
$5R_D$	peak *i*	3261	1.536	0.107	615.9	14.6
	peak *ii*	2001	1.729	0.084	299.4	7.6
$7R_D$	peak *i*	3671	1.543	0.144	939.8	16.2
	peak *ii*	4039	1.736	0.075	533.5	9.1

[a] Each spectrum was fitted using two Gaussian curves of the type: $\delta(E) = \delta_0 \exp[-(E-E_0)^2/\sigma^2]$, where **E** is the photon energy (expressed in eV), δ_0 is the amplitude of the Gaussian, E_0 is the position of its maximum, σ is the width of the Gaussian (defined as the point at which the value is reduced to 1/e of the maximum), and $\delta(E)$ is the value of δ at energy **E**.

[b] Area of each Gaussian curve, defined by: $\delta_0 \times \sigma \times \pi 1/2$.

[c] Transition dipole moments for the transition between state *e* and the two-photon state *e'* (corresponding to peaks *i* or *ii*) as determined from eq. 9 of ref. [1]. The theoretical results for transition dipoles are given in parentheses.

observation that the molecular parameter most strongly affected by the topology of these chromophores is M_{ge}, and not $M_{ee'}$. Moreover, the value of $M_{ee'}(i)$ seems to saturate with the chain length for the longer compound **7R$_D$**. The transitions moments corresponding to peak *ii* are instead smaller than for peak *i*.

Overall, the theoretical predictions are in close agreement with the experiment both for the energetics and the cross-sections in the two-photon spectra, especially when the linewidhts obtained from the fitting of the experimental data are used to define the bandshape in the calculated spectra. It is noteworthy that the quantum chemical calculations predict that dimerization affects weakly the two-photon states, whereas it produces a strong Davydov splitting and red-shift in the linear absorption. The second Davydov component cannot be resolved in the experimental two-photon spectra, but appears as a shoulder on the low energy side of the peak *i* in the theoretical two-photon spectrum of the smallest dimer, **3R$_D$**. Calculations estimate the splittings in the two-photon of **3R$_D$**, **5R$_D$**, and **7R$_D$** to be 0.09, 0.07, and 0.05 eV, respectively. These energies are considerably smaller than those for the linear absorption case but follow the same trend as a function of chain length. These results indicate that intramolecular interactions through the pCp linkage strongly affect the B_u states but weakly perturb the A_g states, because of the transition dipole moments between A_g states are vanishingly small. This absence of strong interchromophore interactions for the two-photon absorption process in the dimer leads to a response that corresponds to additivity of the two monomeric units.

Due to the increased activity and the relative position of the two-photon peaks, the spectra of the **5R**, **5R$_D$** and **7R$_D$** exhibit a broad bandwidth over which the cross section is large. Each of these molecules shows a strong two-photon absorption from about 700 to 850 nm, with a cross section over 700 GM for **5R**, over 1000 GM for **5R$_D$**, and over 2500 GM for **7R$_D$**. This ~ 150 nm bandwidth of the TPA spectra allows for high flexibility in the wavelength used for excitation, which could be a useful feature for applications as two-photon excited fluorescence imaging and optical power limiting. The broad bandwidth may be of use, for example, in multi-probe imaging experiments, in that it gives one a better ability to find a common wavelength for excitation of different TPA dyes that have resolvable fluorescence bands, such that they can be simultaneously excited with a single laser wavelength, but can be imaged separately. Additionally, the spectral region of the TPA spectra of these chromophores overlaps very well with the tuning range of Ti:sapphire lasers, which are a preferred source for two-photon fluorescence microscopy.

Conclusions

A series of compounds in which two conjugated arms are connected through a pCp unit have been synthesizes and characterized as a way to study the electronic interaction between chromophores in a fixed spatial arrangement. The analysis of the linear and two-photon spectroscopic data reveals that the through-space delocalization influences one- and two- photon excitation processes differently. One observes a characteristic Davydov splitting of the monomer linear spectrum into two components in the linear absorption spectra of their respective dimers. In contrast, a splitting is not observed in the two-photon spectra of dimers, and the contributions of the monomers to the cross sections are simply additive. This difference can be rationalized by noting that the linear and two-photon absorption processes involve electronic states of different symmetry. Excited states of monomers with nearly B_u (odd) symmetry participate in the linear absorption, and near A_g (even) symmetry states participate in the two-

photon spectra. For the dimer states, which can be described as belonging to the D_2 point group, the strongest bands in the linear absorption spectra originate from transitions to B_2 and B_3 states. The two-photon spectrum, however, contains essentially transitions to A and B_1 states (the others being much weaker). The absorbed quantum of light induces changes of electronic density within each monomer. The electrostatic interaction between these induced charges leads to the splittings in the electronic spectra of dimers. For the B_2 and B_3 states of the dimer this interaction sums up leading to the large splittings observed in the linear spectra. In the case of dimer A and B_1 states, the individual contributions cancels, giving rise to small splitting of the electronic states is small the two-photon spectra that are insensitive to the close proximity of the two chromophores. Study on a wider series of compounds would be necessary to assess whether the additivity in the two-photon cross section is characteristic of the chromophores studied here or is more general, and to determine how the observed properties depend on the building blocks, their connectivity and the symmetry of the overall structure. In the recent literature, reports can be found of cases where the two-photon cross section increases linearly with the size of a dendrimer or branched structure, as well as of cases where there is a super-linear increase.[17-19]

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B. Provide program statistics as outlined below:

----

(1) Number of PI and Co-PI involved in the research project :   ____4____
(list on an attached page)

(2) Number of Post Doc Supported in the last 12 months under AFOSR:
___7____
(list on an attached page)

(3) Number of graduate students supported in the last 12 months
by AFOSR: ___5____
(list on an attached page)

(4) Other researchers supported in the last 12 months by AFOSR:
___0____
(list on an attached page)

(5) Number of publications by PI's in the last 12 months period in
refereed journals   ___52____

(6) Number of publications in the last 12 months (in refereed journals
only)
that acknowledge AFOSR supports:___12____
(list on an attached page)

(7) Awards and Honors received by the PI (life-time received):
____9 (JWP), 39 (JLB), 3 (BK), 8 (SRM)___
(list on an attached page)

C. Report transitions in the format outlined below. A transition item is
defined as some research results that were used by technology developers
for specific technology development.
a. PI/Institution, b. Item of transition
> (research results being transitioned), c. Transition to (include
> Institution, name and phone number of individual(s)), d. Applications
> which transistion result is being used for)

    a. J. Perry, S. Marder/University of Arizona
    b. New, highly soluble two-photon compounds for near IR optical limiting
    c. AFRL/WPAFB, Dr. Paul Fleitz, (937) 255-3808 x3105
    d. Testing of materials for near IR sensor protection

Lists of Program Statistical Information

(1) List of PI and Co-PI's:
Joseph W. Perry (PI)
Jean-Luc Brèdas
Bernard Kippelen
Seth R. Marder

(2) Number of Post Docs Supported in the last 12 months under AFOSR: 7

JWP: 3
Kathaperumal Mohanalingham (35%)
Cristina Rumi (33%)

JLB: 1
Ohyun Kwon

BK: 1
Benoit Domercq

SRM: 2
Sun-Jae Chung   (33%)
Xiaowei Zhan   (42%)

**(3) Number of graduate students supported in the last 12 months
by AFOSR: ___5___**

JWP: 3
Arianna Biesso (50%)
Wojtek Haske (8%)
Christina Bauer (16%)

JLB: 0

BK: 1
Joshua Haddock

SRM: 1
Aaron Goldberg (33%)

Publications last 12 months:

1. "Five Orders-of-Magnitude Enhancement of Two-Photon Absorption for Dyes on Silver Nanoparticle Fractal Clusters," W. Wenseleers, F. Stellacci, T. Meyer-Friedrichsen, T. Mangel, S. R. Marder, and J. W. Perry, *J.Phys. Chem. B.*, **106**, 6853-6863 (2002).

2. "Laser and Electron-Beam Induced Growth of Nanoparticles for 2 & 3D Metal Patterning," F. Stellacci, C. A. Bauer, T. Meyer-Friedrichsen, W. Wenseleers, V. Alain, S. M. Kuebler, S. J. K. Pond, Y. Zhang, S. R. Marder, and J. W. Perry, *Adv. Mater.* **14**, 194-198 (2002).

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Publications that acknowledge AFOSR support

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11. "Photorefractive polymers sensitized by two-photon absorption," P. A. Blanche, B. Kippelen, A. Schülzgen, C. Fuentes-Hernandez, G. Ramos-Ortiz, J. F. Wang, E. Hendrickx, S. R. Marder, N. Peyghambarian, *Opt. Lett.* **27**, 19-21 (2002).

12. "Photorefractive polymer composites fabricated by injection molding," J. A. Herlocker, C. Fuentes-Hernandez, J. F. Wang, Q. Zhang, S. R. Marder, N. Peyghambarian, and B. Kippelen, *Appl. Phys. Lett.* **80**, 1156-1158 (2002).

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14. "Bis(Dioxaborine) Compounds With Large Two-Photon Cross Sections, And Their Use In The Photodeposition Of Silver", M. Halik, W. Wenseleers, C. Grasso, F. Stellacci, E. Zojer, S. Barlow, J.-L. Bredas, J. W. Perry J. W., S. R. Marder S. R. *Chem. Commun.* 1490-1491 (2003)

15. "Photodegradation Of Selected π-Conjugated Electro-Optic Chromophores", A. Galvan-Gonzalez, K. D. Belfield. G. I. Stegeman, M. Canva, S. R. Marder, K. Staub, G. Levina. R. J.

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16. "Columnar discotic liquid-crystalline oxadiazoles as electron-transport materials", Y.-D. Zhang, K. G. , Jespersen, M. Kempe, J. A. Kornfield, S. Barlow, B. Kippelen,S. R. Marder, *Langmuir*, **19**, 6534-6536 (2003).

17. "Two-Photon Absorption in Three-Dimensional Chromophores Based on [2.2]-Paracyclophane," G. P. Bartholomew, M. Rumi, S. J. K. Pond, J. W. Perry, S. Tretiak and Guillermo C. Bazan, *J. Am. Chem. Soc.*, submitted.

Honors/Awards Lifetime:
Joseph W. Perry
1997-1999 Special Creativity Award, National Science Foundation

1995   Senior Research Scientist, Jet Propulsion Laboratory

1995   Outstanding Chemistry Alumnus, University of South Florida

1992   Medal for Exceptional Scientific Achievement, National Aeronautics and Space Administration

1989   Director's Research Achievement Award, Jet Propulsion Laboratory

1984-85   University of Maryland Foundation Postdoctoral Fellowship at the National Bureau of Standards

1983   Herbert Newby McCoy Award for Excellence in Thesis Research, Division of Chemistry and Chemical Engineering, California Institute of Technology

1976-77   Academic Scholarship, University of South Florida

1973-74   Academic Honors, University of South Florida

Jean-Luc Brédas
➤ Jean Stas Prize, Royal Academy of Belgium, 1980.
➤ Louis Empain Scientific Prize for Chemistry, Empain Foundation - Belgium, 1984.
➤ Louis D'Or Prize of the Royal Society of Sciences of Liège - Belgium, 1985.
➤ Cercle des Alumni Prize for Chemistry and Chemical Engineers, University Foundation - Belgium, 1986.
➤ Folia Theoretica Chimica Acta Prize, 1987.
➤ Prize of the Désiré Jaumain Foundation "Sciences, Art et Culture en Wallonie", 1988.
➤ *Triennal Prize of the Royal Society of Chemistry*, Belgium, 1991.
➤ Appointed "Invited Professor" at Université Catholique de Louvain, 1991-1992.
➤ Holder of the 1993-1994 Chaire Francqui at Facultés Universitaires Notre-Dame de la Paix à Namur (Faculty of Sciences).
➤ Holder of the 1993-1994 Chaire Francqui at Université de Liège (Faculty of Sciences).
➤ *Fellow of the American Physical Society*, elected 1993.
➤ Alphonse Wetrems Prize, Royal Academy of Belgium, 1995.

- Holder of the 1995-1996 Chaire Francqui at the University of Antwerp (Faculty of Sciences).
- Appointed "Invited Professor" at the Institut Supérieur des Matériaux du Mans, Le Mans, France, 1995-1996.
- *President-Elect (1995-1997) and President (1997-1999) of the Royal Society of Chemistry - Belgium (Société Royale de Chimie).*
- Gold Medal of the Université de Mons-Hainaut, 1997.
- Holder of the 1998-1999 Chaire Francqui at Université Catholique de Louvain (Faculty of Applied Sciences).
- *Fellow of the American Association for the Advancement of Science,* elected 1998.
- *Ranked #244 on the list of the 1000 most cited chemists* for the period Jan. 1981 – June 1997 with an average of 27 citations per chemistry paper (source: Institute for Science Information, Philadelphia).
- *Francqui Prize,* 1997.
- *Quinquennial Prize for Exact Sciences of the Belgian National Science Foundation (FNRS),* 2000.
  The Francqui and FNRS Quinquennial Prizes are the two highest scientific prizes in Belgium (and the only ones handed by His Majesty the King).
- *Member of the Royal Academy of Belgium,* elected 1998; Corresponding Member, 1998-2000; Associate Member, 2000-present.
- *Doctor Honoris Causa, University of Linköping,* Sweden, 2000.
- *Italgas Prize for Research and Technological Innovation in Applied Molecular Sciences,* Italgas Foundation, Italy, 2001 (shared with R.H. Friend).
- *Member of the European Research Advisory Board for Science, Technology, and Innovation (EURAB),* 2001-present.
  EURAB is the Science Policy Council reporting to the Commissioner for Research of the European Union (see http://europa.eu.int/comm/research/eurab/index_en.html).
- *Outstanding Honors Faculty Certificate for Teaching,* Honors College, The University of Arizona, 2001.
- Named by the Institute of Science Information (ISI) as one of the top five researchers in the field of conducting polymers, based on the number of citations for the period 1991-2000 (see http://www.esi-topics.com/conducting-polymers/interviews/Jean-Luc-Bredas.html).
  Inclusion (in progress) as one of the ISI Highly Cited Researchers for Chemistry, 2002 (see http://isihighlycited.com).
- *Doctor Honoris Causa, Université Libre de Bruxelles,* Belgium, June 2002.
- Named to the Center for Molecular Science Lectureship at the Institute of Chemistry of the Chinese Academy of Sciences in Beijing, July 2002.
- Named to the Moskowitz Lectureship at the University of Minnesota, November 2002.
- Editor of the "European Journal of Inorganic Chemistry", published by VCH-Wiley, 1998-present.
- Regional Editor of "Synthetic Metals", published by Elsevier Science, 1994-present .
- Member of the Editorial Board of "Materials Science and Engineering", published by Elsevier Science, 1998-present.
- Member of the Advisory Board of "Chemistry of Materials", published by the American Chemical Society, 1997-present.
- Member of the Advisory Board of "Advanced Functional Materials", published by Wiley-VCH, 2000-present.

- Member of the Editorial Board of "Nonlinear Optics", published by Gordon and Breach, Tokyo and New York, 1991-present.
- Member of the Editorial Board for the "Series in Electrically and Optically Active Polymers", published by Marcel Dekker, New York, 1988-1996.
- Member of the Editorial Board of "Chimie Nouvelle", published by the Royal Society of Chemistry of Belgium, 1985-1995.

Bernard Kippelen

2000   NSF CAREER Award

2000   3M Faculty Award

1993-1994 Member of the *Experts Group 21* of the French Ministry of Research and Education.

Seth R. Marder

2004	Fellow, Optical Society of America
2002	Fellow, American Association for the Advancement of Science
5/02	Eastman Kodak, Rochester, NY Weissberger Williams Lecture Series
7/97 - 6/99	NSF Special Creativity Award Extension
2/95	3M Lecturer in Materials Science, University of British Columbia
9/93	Lew Allen Award for Research, The Jet Propulsion Laboratory
7/87 - 11/88	National Research Council Resident Research Associate The Jet Propulsion Laboratory
9/84 - 6/85	W.R. Grace and Company Industrial Fellowship University of Wisconsin at Madison